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The doping concentration dependence of the zinc acceptor ionization energy in $In_{0.49}Ga_{0.51}P$

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The doping concentration dependence of the zinc acceptor energy level in $In_{0.49}Ga_{0.51}P$ has been studied and can be expressed as $E_A = 45.75 - 8.20\times 10^{-6}\,P^{1/3}$ meV, where P is the zinc acceptor concentration in cm^{-3}. The zinc-doped $In_{0.49}Ga_{0.51}P$ epitaxial layers were grown on ⟨100⟩ oriented semi-insulating GaAs substrates which are in very good crystallinity with a lattice mismatch of only 0.26%.

Recently, epitaxial $In_{1-x}Ga_xP$ has become an attractive optoelectronic material due to its potential applications in visible light heterojunction lasers and light emitting diodes.[1–4] It can be grown on GaAs substrates with exact lattice match at a composition of 51% GaP and has a band gap of about 1.9 eV (650 nm in wavelength).

During the growth and characterization of the zinc doped $In_{0.49}Ga_{0.51}P$, we have found that the acceptor ionization energy is dependent on the one-third power of the zinc concentration P. In this report, the relationship is presented and a simple derivation of the relation is obtained by using a two-well Poole–Frenkel potential model.

Zn-doped $In_{0.49}Ga_{0.51}P$ epitaxial layers were grown by liquid-phase-epitaxy method using a graphite slider boat. The substrates were Cr-doped (100) GaAs with etch pit density (EPD) of about 5×10^3 cm^{-2}. The In melt was first baked at 900 °C in a purified H_2 flow of 500 cm^3/min for 10 h. This process is very important to obtain low-carrier concentration and high-photoluminescent intensity in $In_{0.49}Ga_{0.51}P$ epitaxial layers. After the baking process, 48 mg of InP and 18 mg of GaP, both polycrystalline, and an appropriate amount of Zn dopant were added to a 2 g In melt to form the growth solution with a liquidus temperature of 797 °C. The doped epitaxial layers were grown by means of a supercooling technique with 12 °C supersaturation, which is the best growth condition determined previously.[1] The thickness of InGaP epitaxial layers grown during a fixed growth period of 5 min was typically 5 μm. Details of growth conditions and characterization techniques were given elsewhere.[1,5]

When the acceptor concentration becomes higher, the nearest neighbor distance between the acceptor ions becomes shorter, therefore their wave function overlaps. There is strong interaction between them. We assume their potential is of the Poole–Frenkel type, i.e., they interact electrostatically to lower the potential in the midway of the two sites. The potential energy is evaluated from the Bohr radius ($r_B = \hbar^2/m^* e^2$) to infinity. In the practical doping range ($N_A < 5\times 10^{19}$ cm^{-3}), their distance is much larger than r_B. Therefore, the potential can be expressed as[6]

$$V(r) = e/\epsilon_s r, \tag{1}$$

where r is the coordinate of the acceptor atom, ϵ_s the dielectric constant ($12\,\epsilon_0$ for $In_{0.49}Ga_{0.51}P$).[7]

The acceptor state can be described by the Schrodinger equation,

$$[-(\hbar^2/2m^*)\nabla^2 - e/\epsilon_s r]\phi(r) = E\phi(r). \tag{2}$$

The potential wells are depicted in Fig. 1. When the distance between two nearest-neighbor acceptor atoms is $2a$, there is a potential well lowering due to their interaction. The lowering is

$$\Delta E = 2e^2/\epsilon_s a. \tag{3}$$

The original undisturbed impurity ionization energy E_0 is

$$E_0 = (\epsilon_0/\epsilon_s)^2 (m_r/m_0) E_H, \tag{4}$$

where m_r is the reduced effective mass in the valence band ($m_r = 0.62\ m_0$)[7] and E_H ($= 13.6$ eV) the hydrogen ionization energy.

The average distance $2a$ between acceptor atoms is

$$2a = (P)^{-1/3}. \tag{5}$$

Therefore, the actual ionization energy E_A is

$$E_A = \left(\frac{\epsilon_0}{\epsilon_s}\right)^2 \frac{m_r}{m_0} E_H - \frac{4e^2}{\epsilon_s} P^{1/3}. \tag{6}$$

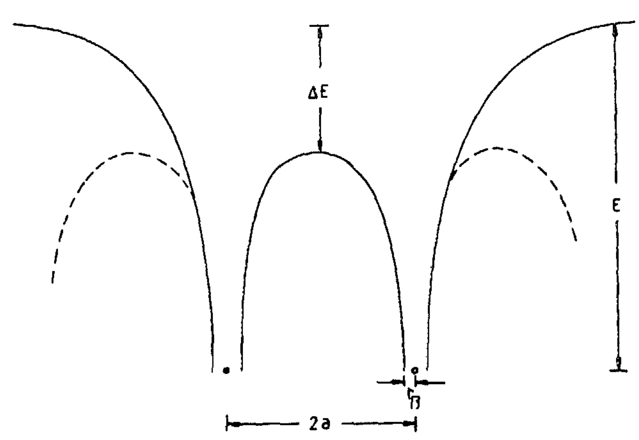

FIG. 1. Two adjacent potential wells which result in a barrier lowering.

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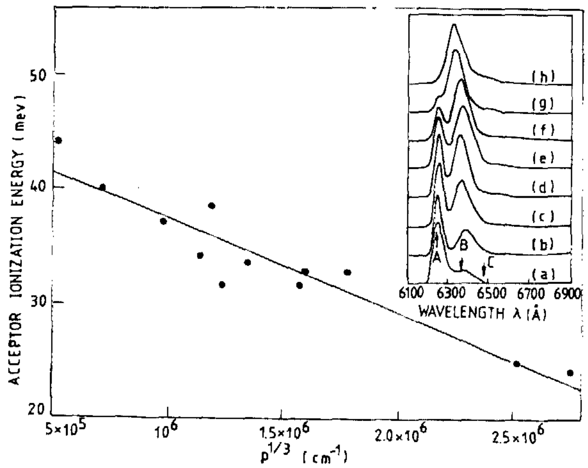

FIG. 2. The experimental acceptor ionization energy in $In_{0.49}Ga_{0.51}P$ vs the cubic root of acceptor doping concentration $P^{1/3}$. The hole concentrations in the inset are (a) 1.4×10^{17}, (b) 3.8×10^{17}, (c) 9.2×10^{17}, (d) 1.5×10^{18}, (e) 2.4×10^{18}, (f) 4.1×10^{18}, (g) 1.6×10^{19}, and (h) 2.1×10^{19} cm^{-3}.

The photoluminescent emission spectra at 14 K of Zn-doped $In_{0.49}Ga_{0.51}P$ layers grown on GaAs are shown in the inset of Fig. 2. Except for the heavily doped sample shown in curve (h), all other samples exhibit two major peaks denoted A and B, and a minor peak denoted C. Peak A is the band-gap emission associated with free electron to free hole recombination. The lower energy peak B is due to conduction band to acceptor level transition which shifts toward peak A with increasing zinc concentrations, thus the zinc level E_A is determined. The weak band C is believed to be a phonon replica of B. Detailed analysis was given in Ref. 5.

The experimental result is $E_A = 45.75\text{–}8.20\times10^{-6}P^{1/3}$ which is fairly close to the calculated value $E_A = 58.55\text{–}6\times10^{-7}\,P^{1/3}$ (in meV). However, a more accurate calculation can be obtained by using the quantum defect method.[8,9]

In conclusion, the doping concentration dependence of zinc acceptor ionization energy E_A has been investigated experimentally. A simple formulation for the ionization energy is obtained

$$E_A = \left(\frac{\epsilon_0}{\epsilon_s}\right)^2 \frac{m_r}{m_0} E_H - \frac{4e^2}{\epsilon_s} P^{1/3},$$

which is in reasonable agreement with the experimental results $E_A = 45.75\text{–}8.20\times10^{-6}\,P^{1/3}$ (in meV).

More detailed calculations require further studies.

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